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(54) Toner image bearing transfer sheet and method for fire fixing toner image using the toner image bearing transfer sheet

(57) A transfer sheet for ceramics has a support, a water-soluble layer formed thereon, and a resin film layer with a thickness of 1 μm or more formed on the water-soluble layer, the resin film layer bearing thereon a toner image which is capable of producing a chromatic color after sintered, and is prepared by an electrophotographic process using a toner which contains a coloring agent, a binder agent, and a fritted glaze. A toner image is fire fixed to a heat-resistant solid surface by forming the toner image on the above-mentioned resin film layer of the transfer sheet by the electrophotographic process using the toner, separating the resin film layer and the toner image together from the support to form a toner-image- bearing resin film member, superimposing the toner-image-bearing resin film member on the heat-resistant solid surface in such a manner that a non-toner-image-bearing side of the resin film member closely adheres to the heat-resistant solid surface, and sintering the toner-image-bearing resin film member at a sintering temperature of the resin film layer or more.

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Description

Field of the Invention

[0001] The present invention relates to a transfer sheet bearing thereon a toner image which is formed by developing a latent electrostatic image using a toner capable of producing a chromatic color after sintered, and more particularly to a transfer sheet which can be effectively used in fire fixing the toner image obtained thereon by an electrophotographic process, in particular, a dry electrophotographic process, to heat-resistant solid surfaces of pottery, glass, enamel, tile, and stone.

[0002] The present invention also relates to a method for fire fixing the toner image to the heat-resistant solid surface using the above-mentioned toner image bearing transfer sheet.

Discussion of Background

[0003] To form an image or pattern on the surface of a heat-resistant solid such as ceramics, a desired image or pattern is directly written on the surface of the heat-resistant solid with a brush using a coloring material comprising an inorganic pigment and a glaze, and thereafter the image bearing heat-resistant solid is subjected to firing at 750 to 1,300°C.

[0004] According to the above-mentioned conventional firing method, some components for use in the coloring material are sintered and the glaze is melted in the course of the firing step, and the inorganic pigment is fixed to the heat-resistant solid surface by the aid of the glaze when cooled to room temperature after sintered. Thus, there remains on the heat-resistant solid surface the image first formed thereon in handwriting.

[0005] The above-mentioned firing method has the drawback that the same image or pattern must be formed in handwriting on a plurality of ceramic products only by a skilled craftsman no matter how simple the image or pattern may be.

[0006] To produce large quantities of ceramic products which bear the same image or pattern thereon, a desired image is first formed on a transfer sheet by screen printing process. The thus formed image-bearing portion is separated from the transfer sheet and attached to the surface of each ceramic product, and then sintered so as to fix the image to the ceramic product.

[0007] The above-mentioned fire fixing method using the screen printing process is proposed, for instance, as disclosed in Japanese Laid-Open Patent Application 49-35407. According to the method disclosed in this application, colored images are formed on the surface of lots of ceramic products in accordance with the following procedure:

[0008] A transfer sheet for use with the fire fixing method comprises a support and a water-soluble paste layer formed thereon. An image is printed by the screen printing process on the above-mentioned water-soluble paste layer of the transfer sheet with an ink composition comprising an inorganic pigment, and thereafter, a water-insoluble resin film layer comprising a vinyl or cellulose-based resin is formed on the printed ink image.

[0009] The image-bearing transfer sheet is immersed into water. The water-soluble paste layer is dissolved in water and the support peels off, whereby there remains an ink-image bearing resin film member.

[0010] The ink-image bearing resin film member thus obtained is applied to the heat-resistant solid surface such as a ceramic plate, and sintered, whereby the sintered image is fixed to the ceramic product.

[0011] According to this method, a large number of ceramic products that bear the same image thereon can be obtained by printing the same image on many transfer sheets by the screen printing, and attaching each of the thus prepared ink-image bearing transfer sheets to the surface of the ceramic product, and sintering the image-bearing ceramic products.

[0012] In the screen printing, however, making of a printing plate for forming the ink image includes many steps and requires a great deal of time and labor. The unit cost is necessarily increased, in particular, when various kinds of items are produced, with each item having the same image thereon. Further, the screen printing process is apt to make worse the working conditions because of the use of organic solvents.

[0013] To solve the problems caused by the screen printing process, there is proposed a method of forming a toner image by the electrophotographic process on the same transfer sheet as employed in the above. To be more specific, an image is formed on the transfer sheet using, for example, a composite powder comprising an organic polymer, an inorganic pigment and a glass component, or a toner comprising a binder resin and a pigment for ceramics. In the same manner as stated in the above, the toner image bearing film member is separated from the support of the transfer sheet and attached to the surface of the ceramic product. Then, the toner image thus attached to the ceramic product is sintered, so that the toner image can be easily fire fixed to the surface of the ceramic product.

[0014] The aforementioned method is disclosed, for example, in Japanese Laid-Open Patent Applications 4-135798, 7-199540, 7-214890, 7-228037, 7-300382, 8-104050, 8-11496, and 8-119668.

[0015] According to the above-mentioned methods using the electrophotographic process, the image formation step can be drastically simplified as compared with that by the screen printing process, and various kinds of items, each item having the same image thereon, can be easily manufactured even though the production of each item is on a small-scale.

[0016] However, the above-mentioned conventional transfer sheet for ceramics comprises a paste layer. Therefore, when the transfer sheet is fed into the electrophotographic copying machine and caused to pass

therethrough for the formation of toner images, there occurs the problem that the paste contained in the transfer sheet adheres to the inside of the copying machine, thereby affecting the transporting performance of the transfer sheet in the copying machine, and the image quality of the obtained toner images.

SUMMARY OF THE INVENTION

[0017] Accordingly, it is a first object of the present invention to provide a transfer sheet for fire fixing a toner image on the heat-resistant solid surface, capable of obtaining a high quality toner image thereon with no difficulty in transporting performance in the electrophotographic copying machine when the toner image is formed on the transfer sheet.

[0018] A second object of the present invention is to provide a method for fire fixing the toner image to the heat-resistant solid surface using the above-mentioned transfer sheet.

[0019] The above-mentioned first object of the present invention can be achieved by a transfer sheet for ceramics comprising a support, a water-soluble layer formed thereon, and a resin film layer with a thickness of 1 μm or more formed on the water-soluble layer, the resin film layer bearing a toner image which is capable of producing a chromatic color after the toner image is sintered, the toner image being prepared by an electrophotographic process using a toner which comprises a coloring agent, a binder agent, and a fritted glaze.

[0020] It is preferable that the resin film layer of the transfer sheet comprise an antistatic agent.

[0021] Further, it is preferable that the resin film layer comprise a pigment.

[0022] The second object of the present invention can be achieved by a method for fire fixing a toner image on a heat-resistant solid surface, the toner image being formed by an electrophotographic process using a toner comprising a coloring agent, a binder agent, and a fritted glaze, and the toner image being capable of producing a chromatic color after the toner image is sintered, the fire fixing method comprising the steps of forming the toner image on a transfer sheet for ceramics which comprises a support, a water-soluble layer formed thereon, and a resin film layer with a thickness of 1 μm or more formed on the water-soluble layer, in such a manner that the resin film layer bears thereon the toner image, separating the resin film layer together with the toner image from the support of the transfer sheet to form a toner-image-bearing resin film member, superimposing the toner-image-bearing resin film member on the heat-resistant solid surface in such a manner that a non-toner-image-bearing side of the toner-image-bearing resin film member comes in contact with the heat-resistant solid surface, and sintering the toner-image-bearing resin film member at a sintering temperature of the resin film layer or more.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0023] As previously pointed out, when toner images are formed using the electrophotographic copying machine on the conventional transfer sheet of which the surface top layer comprises a paste, there occur the problems that the image quality of the obtained toner image is impaired, and the transporting performance of the transfer sheet in the copying machine is lowered.

[0024] As a result of intensive studies about the above-mentioned problems, it has been found that the paste contained in the surface top layer of the transfer sheet is attached to an image transfer drum of the copying machine, thereby producing abnormal toner images on the image transfer drum. Further, the paste for use in the transfer sheet easily adheres to various transporting rollers while the transfer sheet passes through the copying machine, so that these rollers become unfavorably sticky, and fine paper dust and the like are apt to adhere to the sticky rollers. The result is that the transporting rollers do not normally work because of the decreased frictional characteristics thereof.

[0025] In contrast to this, the water-soluble paste layer for use in the transfer sheet according to the present invention is covered with a resin film layer with a thickness of 1 μm or more so as not to bring the paste into direct contact with the inner parts of the electrophotographic copying machine. Therefore, the water-soluble paste contained in the transfer sheet can be prevented from becoming sticky by absorbing moisture in air or water content of the operator's fingers. The transfer sheet of the present invention has no adverse effect on the transporting performance in the copying machine and the image quality of the obtained toner images.

[0026] Examples of the resin for use in the resin film layer of the transfer sheet are cellulose resin, butyral resin, vinyl resin, phenolic resin, urea resin, melamine resin, polyester resin, alkyd resin, polyethylene oxide resin, melamine-alkyd resin, maleic acid resin, acrylate resin, and methacrylate resin. In addition, copolymer resins comprising the monomers for use in the above-mentioned resins are also usable.

[0027] The resin film layer for use in the transfer sheet has a thickness of 1 μm or more, preferably 10 μm or more. When the thickness of the resin film layer is less than 1 μm, the resin film layer is so fragile that the resin film layer is easily torn to get entangled with the roller of the copying machine. Further, when the thickness of the resin film layer is 1 μm or more, it is possible to avoid the exposure of the paste even if there are some defects in the resin film layer.

[0028] The resin film layer may further comprise an antistatic agent. The addition of the antistatic agent to the resin film layer can solve the problem that toner images cannot be favorably formed on the transfer

sheet because of high electrical resistivity of the resin film layer.

[0029] As the antistatic agent for use in the present invention, a cationic surfactant, anionic surfactant, nonionic surfactant, and high-molecular antistatic agent are usable.

[0030] The antistatic agent may be contained in the resin film layer, or coated on the resin film layer to control the electrical resistivity of the transfer sheet. Further, other layers than the resin film layer may comprise the antistatic agent. In this case, the antistatic agent may be contained in the corresponding layer, or coated thereon.

[0031] Furthermore, the resin film layer may comprise a pigment to eliminate the problem of transportation in the electrophotographic copying machine. To be more specific, the friction characteristics of the transfer sheet of which the surface top layer is the above-mentioned resin film layer are different from those of plain paper. Therefore, there is a risk of the transfer sheet according to the present invention causing the transporting trouble in the copying machine. In such a case, it is effective that the pigment be contained in the resin film layer or coated thereon.

[0032] The pigment for use in the present invention is not particularly limited. For example, calcium carbonate, titanium dioxide, talc, and kaolin may be employed. Further, the resin film layer may comprise a frit in order to avoid the transportation problem.

[0033] The toner for use in the present invention, which is capable of producing a chromatic color after sintered, will now be explained in detail.

[0034] The above-mentioned toner capable of producing a chromatic color after sintered herein used is defined as a toner comprising a coloring agent which is capable of retaining the chromatic color even after sintered at 450°C or more.

[0035] The toner for use in the present invention comprises a thermoplastic resin, and a coloring agent such as a pigment for ceramic use, for example, a metallic oxide.

[0036] Examples of the metal element for forming the above-mentioned metallic oxide are Cu, Ag, and Au belonging to the group I in the periodic table; Cd belonging to the group II; Ti belonging to the group IV; V and Sb belonging to the group V; Se, Cr, Mo, W, and U belonging to the group VI; Mn belonging to the group VII; and Fe, Co, Ni, Ir, and Pt belonging to the group VIII. The mixture of the above-mentioned metallic oxides can also be used as the pigment.

[0037] As the coloring agent contained in the toner for use in the present invention, a pigment prepared by mixing a plurality of the above-mentioned metals or metallic oxides, and melting the mixture at a temperature in the range of 1,000 to 1,200°C is particularly preferable. The thus prepared pigment will be hereinafter referred to as an alloy pigment.

[0038] In general, the absorptivity coefficient of the conventional pigment for ceramics is low. Therefore, in order to obtain a full-color toner image with high image density using the toner comprising the above-mentioned conventional pigment for ceramics, it is required to increase the toner deposition amount.

[0039] In contrast to the above-mentioned conventional pigment for ceramics, the alloy pigment shows high absorptivity coefficient. Therefore, when such an alloy pigment is used as the coloring agent for the toner, it is possible to form a full-color toner image with high image density at a small deposition amount of toner.

[0040] Namely, the degree of pigmentation of the alloy pigment is increased. The reason for this is considered to be as follows. The orbit d of a metal element is split by the influence of a plurality of metals, and consequently, the number of electron-transferrable orbits is increased, with the result that the apparent oscillator strength is increased.

[0041] As the thermoplastic resin for use in the toner, any binder resins that are used in conventional toners are usable. Examples of such thermoplastic resins include polyester, polystyrene, polyethylene, polyamide, epoxy resin, epoxy polyol resin, and terpene resin. These resins can be employed alone or in combination. To be more specific, there can be employed a polystyrene resin, a styrene - methyl acrylate copolymer resin, a styrene - ethyl acrylate copolymer resin, and styrene - n-butyl copolymer resin.

[0042] In particular, it is preferable to employ a thermoplastic resin with a sintering temperature in the range of 280 to 360°C.

[0043] It is preferable that the amount ratio of the thermoplastic resin in the toner be in the range of 10 to 40 wt% of the total weight of the toner.

[0044] It is preferable that the toner for use in the present invention comprise a fritted glaze in combination with the above-mentioned coloring agent and thermoplastic resin. In this case, the coloring agent and the fritted glaze may be merely mixed. Alternatively, a mixture of the coloring agent and the fritted glaze may be fused under application of heat thereto, and cooled and pulverized, and the pulverized material thus obtained may be used as the coloring agent.

[0045] In particular, it is preferable to employ a coloring agent which is prepared by mixing the alloy pigment and the fritted glaze in predetermined amounts, fusing the mixture at 650 to 800°C, and thereafter cooling and pulverizing the mixture. By employing such a coloring agent for the toner, a clear full-color toner image with high image density can be formed on the transfer sheet even though the toner deposition amount is small. Finally, when the thus prepared toner-image bearing transfer sheet is attached to the heat-resistant solid surface such as a ceramic product, and sintered, a sintered image with high image density can be clearly formed on the heat-resistant solid surface.

[0046] In the toner composition, it is preferable that the amount ratio by weight of the coloring agent to the

fritted glaze be in the range of 2/8 to 6/4, more preferably in the range of 3/7 to 5/5. When the amount ratio of the coloring agent to the fritted glaze is 2/8 or more, the degree of pigmentation of the toner is sufficient; while when the amount ratio of the coloring agent to the fritted glaze is 6/4 or less, the sintered image can be prevented from peeling away from the surface of the heat-resistant solid.

[0047] The fritted glaze for use in the toner is melted or semi-melted during the sintering step, and thereafter completely solidified when cooled to room temperature, whereby the fritted glaze serves to fire fix the coloring agent contained in the toner to the heat-resistant solid surface.

[0048] Examples of the base material for the fritted glaze include a hydroxide of alkali metal or alkaline earth metal, such as lithium hydroxide; a carbonate of alkali metal or alkaline earth metal, such as lithium carbonate; a chloride of alkali metal or alkaline earth metal and aluminum chloride; boric acid and a borate of a chloride of alkali metal or alkaline earth metal; a metaborate of a chloride of alkali metal or alkaline earth metal; a phosphate of alkali metal or alkaline earth metal; a pyrophosphate of alkali metal or alkaline earth metal; a silicate of alkali metal or alkaline earth metal; a metasilicate of alkali metal or alkaline earth metal; zirconium silicate; bone ash; borax; ammonium metavanadate; metallic oxides such as tungsten oxide, vanadium pentoxide, tin oxide, zirconium oxide, cerium oxide, and molybdenum oxide; metallic fluorides such as calcium fluoride and aluminum fluoride; and glasslet. These materials can be used alone or in combination.

[0049] In order to enhance the bonding between the fritted glaze and the pigment, there can be employed natural minerals, for example, feldspar such as lime feldspar, potash feldspar, soda feldspar and petalite (lithium feldspar), kaolin, siliceous stone, alumina, silica, quartz, titanium oxide, chamotte, earth and ash, limestone, magnesite, talc, and dolomite; and barium carbonate, zinc oxide, and strontium carbonate. These materials may be mixed with the fritted glaze and the pigment in advance, and the obtained mixture may be melted, and thereafter added to the toner composition.

[0050] The toner for use in the present invention may further comprise a charge control agent. As such a charge control agent, there can be employed any of the conventional charge control agents, for example, nigrosine dyes, quaternary ammonium salts, chromium-containing dyes, zinc-containing dyes, iron-containing dyes, molybdic acid chelate pigments, and fluorine-modified quaternary ammonium salts. These charge control agents may be selected depending upon the polarity of the desired toner.

[0051] The amount of charge control agent to be added to the toner composition depends upon the kind of thermoplastic resin, the presence or absence of an additive which may be contained in the toner composition when necessary, and also upon the producing method of the toner including the dispersion process. It is proper that the amount of charge control agent be in the range of 0.1 to 10 parts by weight, more preferably 2 to 6 parts by weight, to 100 parts by weight of the thermoplastic resin.

[0052] When the amount of charge control agent is 0.1 parts by weight or more, the charge quantity of the toner is sufficient, so that scattering of toner particles and the toner deposition on the background can be prevented. When the charge control agent is contained in an amount of 10 parts by weight or less, the electrostatic attraction of the toner to the carrier is proper, so that the increase in fluidity of the developer can be prevented and the decrease in image density can be reduced.

[0053] Also, other conventional additives, for example, an agent for improving the toner fluidity such as hydrophobic silica, zinc stearate, aluminum stearate or titanium oxide, may be added to the toner composition for use in the present invention.

[0054] In the present invention, the above-mentioned toner capable of producing a chromatic color after sintered can be used as a one-component developer for developing a latent electrostatic image. Further, the toner may be used together with a carrier for the two-component developer.

[0055] As the carrier for forming a two-component developer, the conventional carrier particles, such as iron particles, ferrite particles, and glass beads can be employed. Those carrier particles may be coated with a resin, such as poly(carbon fluoride), poly(vinyl chloride), poly(vinylidene chloride), phenolic resin, poly(vinyl acetal), or silicone resin.

[0056] It is preferable that the amount of the toner be in the range of about 1 to 30 parts by weight, more preferably 8 to 16 parts by weight, to 100 parts by weight of the carrier.

[0057] The method for fire fixing the toner image on a heat-resistant solid surface such as a ceramic product using the above-mentioned transfer sheet comprises the steps of:

(1) forming a toner image by an electrophotographic process on the transfer sheet wherein a water-soluble layer and a resin film layer (for example, made of acrylic resin or polystyrene resin) are successively overlaid on a support in such a manner that the resin film layer bears thereon the toner image,

(2) separating the resin film layer together with the toner image from the support to prepare a toner-image-bearing resin film member by immersing the toner image bearing transfer sheet in water to dissolve the water-soluble layer,

(3) superimposing the toner-image-bearing resin film meter on the heat-resistant solid surface in such a manner that a non-toner-image-bearing side of the toner-image-bearing resin film member

comes in contact with the heat-resistant solid surface, and

(4) sintering the toner-image-bearing resin film member, thereby fire fixing the toner image to the heat-resistant solid surface.

[0058] The resin film layer for use in the transfer sheet may have a sintering temperature of 330 to 350°C.

[0059] The specific method for fire fixing the toner image to the heat-resistant solid may be appropriately determined depending upon the position of an image to be formed in the heat-resistant solid, that is, the surface portion of the heat-resistant solid or somewhat inner portion thereof. In any case, an electric oven or a gas oven is usable.

[0060] Namely, to obtain the sintered image on the surface portion of the heat-resistant solid, for instance, the temperature in an electric or gas oven is gradually increased from room temperature to 750 to 850°C by approximately 200°C/hour, and the temperature is maintained at 750 to 850°C for about 30 minutes to one hour. Thereafter, the oven is cooled to room temperature, and the image bearing heat-resistant solid is taken out of the oven. During the above-mentioned sintering step, the coloring agent contained in the toner is fire fixed to the surface portion of the heat-resistant solid by the action of the fritted glaze also contained in the toner. Thus, there can be obtained the heat-resistant solid surface with a fire fixed image.

[0061] On the other hand, to form an image in an inner portion of the heat-resistant solid, for instance, the temperature in an electric or gas oven is gradually increased from room temperature to 1100 to 1300°C by approximately 200°C/hour, and the temperature is maintained at 1100 to 1300°C for 30 minutes to one hour. Thereafter, the oven is cooled to room temperature, and the image bearing heat-resistant solid is taken out of the oven. In the above-mentioned sintering step, the temperature is not always necessarily raised from room temperature. However, there is a risk of the heat-resistant solid being cracked or deformed in the sintering step when the heat-resistant solid suffers a rapid change in temperature in the heating or cooling process. The occurrence ratio of such a risk slightly varies depending upon the thickness and the kind of heat-resistant solid. Therefore, it is preferable that the increase or decrease rate of temperature in the oven be in the range of 50 to 500°C/hour, more preferably 100 to 300°C/hour. When the increase or decrease rate of temperature is within the range of 50 to 500°C/hour, production efficiency is not lowered, and the heat-resistant solid can be fired uniformly without any deformation.

[0062] Other features of this invention will become apparent in the course of the following description of exemplary embodiments, which are given for illustration of the invention and are not intended to be limiting thereof.

Example 1

1. Preparation of Two-component Developers

(Preparation of fritted glaze)

[0063] A mixture of 80 g of Al_2O_3, 370 g of SiO_2, 50 g of Na_2O, and 500 g of PbO was pulverized in a stamp mill and blended in a Henschel mixer, and the thus obtained mixture was sintered at 1200°C and pulverized. Thus, a fritted glaze was obtained.

(Preparation of black coloring agent)

[0064] A mixture of 110 g of Cr_2O_3, 270 g of MnO, 112 g of Fe_2O_3, and 508 g of Co_2O_3 was pulverized in a stamp mill and blended in a Henschel mixer, and the thus obtained mixture was sintered at 1100°C and pulverized.

[0065] Then, 300 g of the thus pulverized mixture and 500 g of the above obtained fritted glaze were blended in the Henschel mixer, and the resultant mixture was sintered at 750°C, and pulverized. Thus, a black coloring agent comprising the alloy pigment was obtained.

(Preparation of yellow coloring agent)

[0066] A mixture of 10 g of CuO, 190 g of ZnO, and 800 g of Sb_2O_3 was pulverized in a stamp mill and blended in a Henschel mixer, and the thus obtained mixture was sintered at 1100°C and pulverized.

[0067] Then, 300 g of the thus pulverized mixture and 500 g of the above obtained fritted glaze were blended in the Henschel mixer, and the resultant mixture was sintered at 750°C, and pulverized. Thus, a yellow coloring agent comprising the alloy pigment was obtained.

(Preparation of magenta coloring agent)

[0068] A mixture of 160 g of Fe_2O_3, 40 g of NiO, 40 g of CuO, and 760 g of Au_2O was pulverized in a stamp mill and blended in a Henschel mixer, and the thus obtained mixture was sintered at 1100°C and pulverized.

[0069] Then, 300 g of the thus pulverized mixture and 500 g of the above obtained fritted glaze were blended in the Henschel mixer, and the resultant mixture was sintered at 750°C, and pulverized. Thus, a magenta coloring agent comprising the alloy pigment was obtained.

(Preparation of cyan coloring agent)

[0070] A mixture of 170 g of Cr_2O_3, 10 g of Fe_2O_3, 690 g of Co_2O_3, and 130 g of ZnO was pulverized in a stamp mill and blended in a Henschel mixer, and the

thus obtained mixture was sintered at 1100°C and pulverized.

[0071] Then, 300 g of the thus pulverized mixture and 500 g of the above obtained fritted glaze were blended in the Henschel mixer, and the resultant mixture was sintered at 750°C, and pulverized. Thus, a cyan coloring agent comprising the alloy pigment was obtained.

⟨Preparation of black, yellow, magenta, and cyan toners⟩

[0072] 100 parts by weight of a styrene - methyl acrylate copolymer resin (Tg=54°C), 4 parts by weight of a commercially available zinc salicylate derivative "Bontron E84" (Trademark), made by Orient Chemical Industries, Ltd., and 230 parts by weight of the above prepared black coloring agent were mixed in a mixer, and kneaded and fused in a two-roll mill. After the kneaded mixture was rolled and cooled, the resultant mixture was pulverized and the pulverized material was classified to obtain a black toner with a volume mean diameter of 9.3 μm.

[0073] The procedure for preparation of the black toner as mentioned above was repeated except that the black coloring agent used in the preparation of the black toner was respectively replaced by the yellow coloring agent, magenta coloring agent, and cyan coloring agent, whereby a yellow toner, a magenta toner, and a cyan toner were obtained. The volume mean diameter of the yellow toner was 9.3 μm; that of the magenta toner, 9.1 μm; and that of the cyan toner, 9.0 μm.

⟨Preparation of black, yellow, magenta, and cyan developers⟩

[0074] Further, a commercially available hydrophobic silica (Trademark "R972", made by Nippon Aerosil Co., Ltd.) was added in an amount of 0.5 wt% to the above prepared black toner. The resultant mixture was stirred using a mixer.

[0075] 100 parts by weight of a silicone resin (Trademark "KR50" made by Shin-Etsu Chemical Co., Ltd.), 3 parts by weight of carbon black (Trademark "BP2000" made by Cabot Corporation), and 100 parts by weight of toluene were dispersed in a homomixer for 30 minutes, whereby a coating layer formation liquid for carrier was prepared.

[0076] The above prepared coating layer formation liquid and 1000 parts by weight of spherical ferrite particles with an average particle diameter of 70 μm were placed in a fluidized bed type coating apparatus so as to provide a coating layer on the spherical ferrite particles. Thus, a resin-coated carrier was prepared.

[0077] A mixture of 90 g of the above prepared black toner and 910 g of the resin-coated carrier was stirred in a ball mill for 30 minutes, whereby a black developer was obtained.

[0078] The procedure for preparation of the black developer as mentioned above was repeated except that the black toner was replaced by the yellow toner, so that a yellow developer was obtained.

[0079] The procedure for preparation of the black developer as mentioned above was repeated except that the black toner was replaced by the magenta toner, so that a magenta developer was obtained.

[0080] The procedure for preparation of the black developer as mentioned above was repeated except that the black toner was replaced by the cyan toner, so that a cyan developer was obtained.

2. Preparation of transfer sheet

[0081] An aqueous solution of dextrin was coated on the surface of a single-sided enamelled paper with a basis weight of 90 g/m^2 so as to provide a dextrin layer with a thickness of 20 μm on a dry basis.

[0082] A coating liquid prepared by dissolving an ethyl cellulose resin (Trademark "N-22", made by Hercules Incorporated) in a mixed solvent of toluene and ethyl alcohol was coated on the above prepared dextrin layer so as to provide an ethyl cellulose resin film layer with a thickness of 15 μm on a dry basis.

[0083] Thus, a transfer sheet No. 1 according to the present invention was obtained.

3. Formation of toner image on transfer sheet

[0084] The above obtained black, yellow, magenta, and cyan developers, each in an amount of 450 g, were set in the respective color development units of a commercially available electrophotographic color copying machine (Trademark "PRETER 650" made by Ricoh Company, Ltd.). A full-color toner image was formed on the above-mentioned ethyl cellulose resin film layer of the transfer sheet No. 1 under the following electrophotographic conditions:

[Electrophotographic conditions]

[0085]

Feeding speed of transfer sheet: 180 mm/sec
Charging potential: -650 V
Potential after exposure: -100 to -500 V
Developing bias: -500 V
Transfer bias for belt: 1400 to 1700 V
Transfer bias for transfer sheet: 900 to 1500 V
Temperature of image fixing roller: 180°C

[0086] The ambient temperature and relative humidity were respectively controlled to 30°C and 85% during the image formation. Ten transfer sheets were fed into the copying machine one by one from a manual paper feeder thereof, and subjected to image formation. During the image formation of ten transfer sheets, there

occurred no trouble concerning the transportation of the transfer sheets in the copying machine. In addition, clear toner images were formed on all the transfer sheets.

4. Fire fixing of toner image to heat-resistant solid surface

[0087] The toner-image-bearing transfer sheet thus obtained was immersed into water, so that the toner-image-bearing ethyl cellulose resin film layer was separated from the support of the transfer sheet. The thus formed toner-image-bearing resin film member was then attached to a commercially available tile (Trademark "RS252/1001" made by INAX Co., Ltd.) in such a manner that a non-toner-image-bearing side of the toner-image-bearing resin film member closely adhered to the tile.

[0088] The toner-image-bearing tile was gradually heated to 800°C at an increase rate of 100°C/hour, and maintained at 800°C for 30 minutes, and thereafter cooled to room temperature, whereby a toner image was fire fixed to the tile. The sintered image on the tile was excellent.

Example 2

[0089] The procedure for formation of the transfer sheet No. 1 in Example 1 was repeated except that the thickness of the ethyl cellulose resin film layer of the transfer sheet No. 1 prepared in Example 1 was changed from 15 to 2 μm. Thus, a transfer sheet No. 2 according to the present invention was obtained.

[0090] Using the same electrophotographic copying machine as employed in Example 1, a full-color toner image was formed on the above-mentioned transfer sheet No. 2 under the same conditions as in Example 1.

[0091] While the toner images were continuously formed on ten of the transfer sheets No. 2, there occurred no trouble concerning the transportation in the copying machine. In addition, clear toner images were formed on all the transfer sheets.

[0092] Using the toner-image-bearing transfer sheet thus obtained, the toner image was fire fixed to the commercially available tile (Trademark "RS252/1001" made by INAX Co., Ltd.) in the same manner as in Example 1. The result was that the sintered image on the tile was excellent.

Example 3

[0093] The procedure for formation of the transfer sheet No. 1 in Example 1 was repeated except that the ethyl cellulose resin film layer for use in the transfer sheet No. 1 prepared in Example 1 was replaced by a butyral resin film layer with a thickness of 15 μm. Thus, a transfer sheet No. 3 according to the present invention was obtained.

[0094] Using the same electrophotographic copying machine as employed in Example 1, a full-color toner image was formed on the above-mentioned transfer sheet No. 3 under the same conditions as in Example 1.

[0095] While the toner images were continuously formed on ten of the transfer sheets No. 3, there occurred no trouble concerning the transportation in the copying machine. In addition, clear toner images were formed on all the transfer sheets.

[0096] Using the toner-image-bearing transfer sheet thus obtained, the toner image was fire fixed to the commercially available tile (Trademark "RS252/1001" made by INAX Co., Ltd.) in the same manner as in Example 1. The result was that the sintered image on the tile was excellent.

Example 4

[0097] The procedure for formation of the transfer sheet No. 1 in Example 1 was repeated except that a commercially available antistatic agent (Trademark "Chemistat 2500", made by Sanyo Chemical Industries, Ltd.) was added to the ethyl cellulose resin solution for forming the ethyl cellulose resin film layer employed in Example 1 in an amount of 20 wt% of the ethyl cellulose resin. Thus, a transfer sheet No. 4 according to the present invention was obtained.

[0098] Using the same electrophotographic copying machine as employed in Example 1, a full-color toner image was formed on the above-mentioned transfer sheet No. 4 under the same conditions as in Example 1 except that the ambient temperature and humidity were respectively changed to 10°C and 20%RH.

[0099] While the toner images were continuously formed on ten of the transfer sheets No. 4, three transfer sheets caused the paper feeding trouble in the copying machine. However, clear toner images were formed on all the ten transfer sheets.

[0100] Using the toner-image-bearing transfer sheet thus obtained, the toner image was fire fixed to the commercially available tile (Trademark "RS252/1001" made by INAX Co., Ltd.) in the same manner as in Example 1. The result was that the sintered image on the tile was excellent.

Example 5

[0101] The procedure for formation of the transfer sheet No. 4 in Example 4 was repeated except that a frit was added to the ethyl cellulose resin solution for forming the ethyl cellulose resin film layer employed in Example 4 in an amount of 40 wt% of the ethyl cellulose resin. Thus, a transfer sheet No. 5 according to the present invention was obtained.

[0102] Using the same electrophotographic copying machine as employed in Example 1, a full-color toner image was formed on the above-mentioned transfer sheet No. 5 under the same conditions as in Example 4.

[0103] While the toner images were continuously formed on ten of the transfer sheets No. 5, such a paper feeding trouble as observed in Example 4 did not occur. In addition, clear toner images were formed on all the ten transfer sheets.

[0104] Using the toner-image-bearing transfer sheet thus obtained, the toner image was fire fixed to the commercially available tile (Trademark "RS252/1001" made by INAX Co., Ltd.) in the same manner as in Example 1. The result was that the sintered image on the tile was excellent.

Comparative Example 1

[0105] The procedure for formation of the transfer sheet No. 1 in Example 1 was repeated except that the ethyl cellulose resin film layer was not provided on the dextrin layer. Thus, a comparative transfer sheet No. 1 was obtained.

[0106]. Using the same electrophotographic copying machine as employed in Example 1, a full-color toner image was formed on the above-mentioned comparative transfer sheet No. 1 under the same conditions as in Example 1.

[0107] While the toner images were continuously formed on ten of the comparative transfer sheets No. 1, paper jam and paper feeding trouble took place in the copying machine. The reason for this was that the transfer sheets adhered to each other because of exposure of the dextrin, so that the transfer sheets were apt to stick to the rollers provided in the copying machine. However, there was no conspicuously abnormal toner image on the transfer sheets.

[0108] On the toner image formed on the comparative transfer sheet No. 1, a butyral resin solution was coated and dried to form a butyral resin film on the toner image. The toner-image-bearing transfer sheet thus obtained was immersed into water, and the toner image supported by the butyral resin film was separated from the support of the transfer sheet. The thus formed toner-image-bearing butyral resin film was then attached to the commercially available tile (Trademark "RS252/1001" made by INAX Co., Ltd.) in such a manner that the butyral resin film side closely adhered to the tile.

[0109] The toner-image-bearing tile was sintered and the toner image was fire fixed in the same manner as in Example 1. The result was that the sintered image on the tile was not poor.

Comparative Example 2

[0110] The procedure for formation of the transfer sheet No. 1 in Example 1 was repeated except that the thickness of the ethyl cellulose resin film layer of the transfer sheet No. 1 prepared in Example 1 was changed from 15 to 0.5 µm. Thus, a comparative transfer sheet No. 2 was obtained.

[0111] Using the same electrophotographic copying machine as employed in Example 1, a full-color toner image was formed on the above-mentioned comparative transfer sheet No. 2 under the same conditions as in Example 1.

[0112] While the toner images were continuously formed on ten of the comparative transfer sheets No. 2, there occurred no trouble concerning the transportation in the copying machine. However, the ethyl cellulose resin film layer of each transfer sheet became creased and cracked, so that the quality of toner images formed on the transfer sheets was poor.

[0113] Thereafter, the toner-image-bearing resin film member was prepared and attached to the commercially available tile (Trademark "RS252/1001" made by INAX Co., Ltd.) in the same manner as in Example 1. When the toner-image-bearing tile was sintered, the ethyl cellulose resin film layer of the toner-image-bearing resin film member was torn in the course of image transfer to the tile, and consequently, the toner image was not fire fixed to the tile.

Claims

1. A transfer sheet for ceramics comprising:

   a support,
   a water-soluble layer formed thereon, and
   a resin film layer with a thickness of 1 µm or more formed on said water-soluble layer, said resin film layer bearing a toner image which is capable of producing a chromatic color after said toner image is sintered, said toner image being prepared by an electrophotographic process using a toner which comprises a coloring agent, a binder agent, and a fritted glaze.

2. The toner image bearing transfer sheet as claimed in Claim 1, wherein said resin film layer comprises an antistatic agent.

3. The toner image bearing transfer sheet as claimed in Claim 1 or 2, wherein said resin film layer comprises a pigment.

4. A method for fire fixing a toner image on a heat-resistant solid surface, said toner image being formed by an electrophotographic process using a toner comprising a coloring agent, a binder agent, and a fritted glaze, and said toner image being capable of producing a chromatic color after said toner image is sintered, said method comprising the steps of:

   forming said toner image on a transfer sheet for ceramics which comprises a support, a water-soluble layer formed thereon, and a resin film layer with a thickness of 1 µm or more formed

on said water-soluble layer, in such a manner that said resin film layer bears thereon said toner image,

separating said resin film layer together with said toner image from said support of said transfer sheet to form a toner-image-bearing resin film member,

superimposing said toner-image-bearing resin film member on said heat-resistant solid surface in such a manner that a non-toner-image-bearing side of said toner-image-bearing resin film member comes in contact with said heat-resistant solid surface, and

sintering said toner-image-bearing resin film member at a sintering temperature of said resin film layer or more.

5. The fire fixing method as claimed in Claim 4, wherein said resin film layer of said transfer sheet comprises an antistatic agent.

6. The fire fixing method as claimed in Claim 4 or 5, wherein said resin film layer of said transfer sheet comprises a pigment.